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employed in epoxy resins in order to achieve particular levels of thermal conductivity.

Anti-friction coatings for titanium which comprise molybdenum disulfide are known from U.S. Pat. No. 4,329, 238. These coatings are employed in the form of an anti-friction paste containing epoxy resin, molybdenum disulfide, graphite, aluminum, copper, alumosilicate and polyethylene polyamine curing agent. This paste provides low friction as well as reduced wear and extended service life to the devices coated therewith.

U.S. Pat. No. 5,160,243 discloses turbine blades provided with a wear resistant coating which includes molybdenum disulfide. The patent also mentions the potential for using a coating including Teflon®, bentonite, inorganic oxide particles and an epoxy material although no examples of this 15 coating are given.

Accordingly, although several coatings are known for titanium and its alloys, there remains a need in the art for an anti-wear coating for titanium and its alloys which can withstand tribological conditions.

## SUMMARY OF THE INVENTION

The primary object of the present invention is to provide protection from wear and surface damage for titanium and its alloys when employed in tribological applications under boundary lubrication conditions.

In order to meet this objective, the present invention provides a friction and wear resistant coated titanium or titanium alloy which includes a titanium or titanium alloy substrate, a first layer of  $Ti_xO_y$  bonded to a surface of the titanium of titanium alloy substrate and a second layer comprising a cured epoxy resin bonded to the first layer. It has been found that these coatings significantly reduce the wear and the coefficient of friction for titanium and its alloys when its slides on an uncoated harder alloy. In this manner the durability of the protected titanium or titanium alloy can be significantly improved.

Another object of the present invention is to provide methods for protecting titanium and its alloys from severe 40 wear and high friction. This objective is met by forming a Ti<sub>x</sub>O<sub>y</sub> layer on the surface of the titanium or titanium alloy, coating the Ti<sub>x</sub>O<sub>y</sub> layer with a composition comprising an epoxy resin and curing the epoxy resin with an epoxy resin curing agent.

Other objects and advantages of the present invention will be apparent from the detailed description which follows.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a graphical representation of the friction coefficient of a coated Ti—6Al—4V ball in contact with coated Ti—6Al—4V flats in polypropylene oxide lubricant in accordance with the invention.

FIG. 1B is a graphical representation of the friction coefficient of an uncoated Ti—6Al—4V ball in contact with a coated Ti—6Al—4V flat using a polypropylene oxide lubricant.

FIG. 1C is a graphical representation of the friction coefficient of an uncoated Ti—6Al—4V ball in contact with an uncoated Ti—6Al—4V flat using a polyphenylene oxide lubricant.

## DETAILED DESCRIPTION OF THE INVENTION

In a first aspect, the present invention relates to a wear resistant coated titanium or titanium alloy. The coating includes two layers of material, a first layer of a titanium oxide and a second layer of cured epoxy resin bonded to the first layer of titanium oxide.

The titanium oxide layer may include titanium oxides of the formula  $\text{Ti}_{x}O_{y}$  wherein x is 1–2 and y is 1–3. Preferably, this titanium oxide layer is an extremely thin surface layer of titanium dioxide.

The titanium oxide layer on the surface of the titanium or the titanium alloy serves as a cross-linking bridge to improve the adherence of the epoxy coating to the surface of the titanium or titanium alloy. The titanium oxide layer may be formed by conventional methods for the hydrolysis of a titanium orthoester. In particular, the surface of the titanium or the titanium alloy is treated with a tetraalkyl titanate in order to form a layer comprising titanium oxide on the surface of the titanium or titanium alloy. The tetraalkyl titanate may be, for example, tetra-n-butyl titanate and is typically employed in the form of a solution in an organic solvent such as heptane.

The titanium oxide layer is formed by subjecting a clean surface of the titanium or titanium alloy to immersion in the solution of tetraalkyl titanate, evaporating the solvent and hydrolyzing the remaining tetraalkyl titanate typically by the presence of moisture in the air to form a thin, dense network of a titanium oxide film. Once the titanium oxide layer has been applied, the coated substrate may be immersed in liquid epoxy resin to which an epoxy curing agent has been added. Typically, 20% by weight of the liquid resin mixture is curing agent.

Preferred epoxy resins which are useful in the present invention are 2–3 epoxypropylether epoxy resins such as N-butylglycidylether and 4.4'-isopropylidene-bis-phenyl diglycydylether. Other types of epoxy resins such as epoxynovolac resins can be employed. Multi-functional resins containing two or four epoxy groups per molecule are preferred since they permit upgrading of thermal stability, chemical resistance and the electrical and mechanical properties of the coatings.

The epoxy curing agent to be employed may be selected from conventional epoxy agents for the particular epoxy that is employed in the coating. Thus, for glycydylethers, amine curing agents such as diethylene triamine, triethylene tetraamine and polyoxypropylene diamine may be employed. For epoxy-novolac resins a typical curing agent is 2-ethyl-4-methylimidazole. The best epoxy resins for the present invention are epoxy resins which are highly reactive towards the titanium oxide layer. In particular, 2,3-epoxypropyl resins are most preferred for this reason.

The two layer coating of titanium oxide and epoxy reduces wear and provides an excellent reduction in the friction coefficient. It is possible to further increase the wear resistance of the epoxy coating by adding a wear resistant filler material to the coating. Typical wear resistant filler materials are diamond powder, boron nitride powder, silicon carbide powder, corundum, ceramic wool, ceramic spheres, zinc oxide, alumosilicate, silica, titanium dioxide and alumina.

The wear resistant filler material may comprise 0.1–50 parts by weight, based on the weight of the epoxy coating, and more preferably comprises 1–5 parts by weight, based on the weight of the coating. The most preferred wear resistant filler material is diamond powder having a particle size of less than 1 micron.

In a second aspect, the present invention relates to a method for the protection of titanium and its alloys from severe wear and high friction under tribological conditions.

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